

DMFT Study for Valence Fluctuations in the Extended Periodic Anderson Model

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Abstract. We study valence fluctuations at finite temperatures in the extended periodic Anderson model, where the Coulomb interaction between conduction and localized f -electrons is taken into account, using dynamical mean-field theory combined with the continuous-time quantum Monte Carlo (CT-QMC) method. The valence transition with the hysteresis is clearly found, indicating the first-order phase transition between the Kondo and mixed-valence states. We demonstrate that spin correlation rapidly develops when the system approaches the valence transition point. The comparison of the impurity solvers, the CT-QMC, non-crossing approximation, and one-crossing approximation, is also addressed.

1. Introduction

Heavy fermion systems with rare-earth or actinide elements have attracted considerable attention. One of the interesting phenomena in the systems is the valence transition, where the valence in rare-earth ions abruptly changes due to applied field and/or pressure. Recently, it has been suggested that the superconductivity in the rare-earth compound CeCu_2Si_2 [1] and quantum critical behavior in the quasicrystal $\text{Au}_{51}\text{Al}_{34}\text{Yb}_{15}$ [2] are related to valence fluctuations. These stimulate further theoretical and experimental investigations on valence fluctuations in the heavy-fermion systems [3–8].

Valence fluctuations and valence transitions have been studied theoretically in terms of the extended periodic Anderson model (EPAM) [9–15]. The possibility of the valence transition in this model has been suggested by the slave boson mean-field theory [12], density matrix renormalization group [10], and dynamical mean-field theory (DMFT) [11, 15]. Although the jump singularity in the curve of the f -electron number has been reported in several papers [10–15], the hysteresis has not been found clearly. Therefore, it is instructive to examine carefully this problem by means of unbiased numerical methods.

Motivated by this, we study the EPAM at finite temperatures, combining DMFT with a continuous-time quantum Monte Carlo (CT-QMC) method [26–28], which is one of the most powerful numerical techniques. We clarify that the first-order valence transition occurs with a hysteresis in the curve of the valence. We also compare the CT-QMC results with those obtained by the non-crossing approximation (NCA) [23–25] and the one-crossing approximation (OCA) [25], and discuss the advantage of the CT-QMC method.

This paper is organized as follows. In Sec. 2, we introduce the model Hamiltonian and summarize our numerical method briefly. In Sec. 3, we demonstrate the valence transition at finite temperatures in the framework of DMFT with the CT-QMC methods. We also discuss

spin correlation in the vicinity of the valence transition. Furthermore, quantitative discussions for the valence transition in the EPAM are given in Sec. 4, by comparing with the DMFT results obtained by means of the CT-QMC, NCA, and OCA impurity solvers. In the final section, we state our conclusions.

2. Model and Method

We study valence fluctuations at finite temperatures in the EPAM, which should be described by the following Hamiltonian:

$$H_{\text{EPAM}} = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + V \sum_{i, \sigma} (c_{i\sigma}^\dagger f_{i\sigma} + \text{h.c.}) + \epsilon_f \sum_{i, \sigma} n_{i\sigma}^f + U_{ff} \sum_i n_{i\uparrow}^f n_{i\downarrow}^f + U_{cf} \sum_{i, \sigma, \sigma'} n_{i\sigma}^c n_{i\sigma'}^f, \quad (1)$$

where $c_{i\sigma}$ ($f_{i\sigma}$) is the annihilation operator of a conduction electron (f -electron) with spin $\sigma (= \uparrow, \downarrow)$. $n_{i\sigma}^c (= c_{i\sigma}^\dagger c_{i\sigma})$ and $n_{i\sigma}^f (= f_{i\sigma}^\dagger f_{i\sigma})$ are the number operators of the conduction and the f -electrons at i th site, respectively. t is the hopping integral of the conduction electrons between the nearest-neighbor sites, V is the hybridization between the conduction band and the f -orbitals, and ϵ_f is the energy level of the f -orbitals. U_{ff} is the repulsive interaction between the f -electrons and U_{cf} is the repulsive interaction between the conduction and the f -electrons. We here consider the Bethe lattice with a large coordination number $z \rightarrow \infty$, which has a semi-elliptic density of states with the bandwidth $2D$.

To study low temperature properties in the EPAM [16, 17], we make use of DMFT [18–21]. In the framework of DMFT, the lattice model is mapped to an effective impurity model, where local electron correlations are taken into account precisely. This method is formally exact in the infinite dimensions and has successfully been used even in three dimensions. The site-diagonal lattice Green's function is required to be equal to the Green's function of the effective impurity model. This condition leads to the self-consistent equation [22], as

$$[\hat{\mathcal{G}}_\sigma^{-1}(\omega)]_{cc} = i\omega - \mu - \left(\frac{D}{2}\right)^2 [\hat{G}_{\text{imp}\sigma}(\omega)]_{cc}, \quad (2)$$

where μ is the chemical potential, $\hat{\mathcal{G}}_\sigma(\omega)$ [$\hat{G}_{\text{imp}\sigma}(\omega)$] is the noninteracting (full) impurity Green's function with spin σ . To solve the effective impurity model, we make use of the CT-QMC method based on the hybridization expansion [26–28]. In this method, the partition function is described by the expansion in powers of the impurity-bath mixing, which allows us to evaluate physical quantities quantitatively in terms of the Monte Carlo procedure. This is contrast to other biased methods such as the NCA and OCA methods. In the paper, we set $U_{ff}/D = 20$ and $U_{cf}/D = 8$, and use the half bandwidth D as the unit of energy.

3. First-order valence transition

Now, we study the EPAM at finite temperatures to clarify how valence fluctuations develop in the system. To characterize the Kondo and mixed-valence states, we first examine the particle number when the chemical potential is varied. In Fig. 1, we show the total particle number per site $\langle n_{\text{tot}} \rangle$ and the f -electron number per site $\langle n_f \rangle$ when $T/D = 0.04$ and $V/D = 0.13$. In the case of $\epsilon_f/D = -7.8$, the total particle number increases monotonically with increase of the chemical potential as shown in Fig. 1(a) whereas the f -electron number little changes within $7.7 < \mu/D < 8.0$ as shown in Fig. 1(d). This indicates that the Kondo state is stabilized with localized electrons in the f -orbitals. On the other hand, we find in Figs. 1(c) and 1(f) that both $\langle n_{\text{tot}} \rangle$ and $\langle n_f \rangle$ are smoothly changed in the case $\epsilon_f/D = -7.45$. This implies that

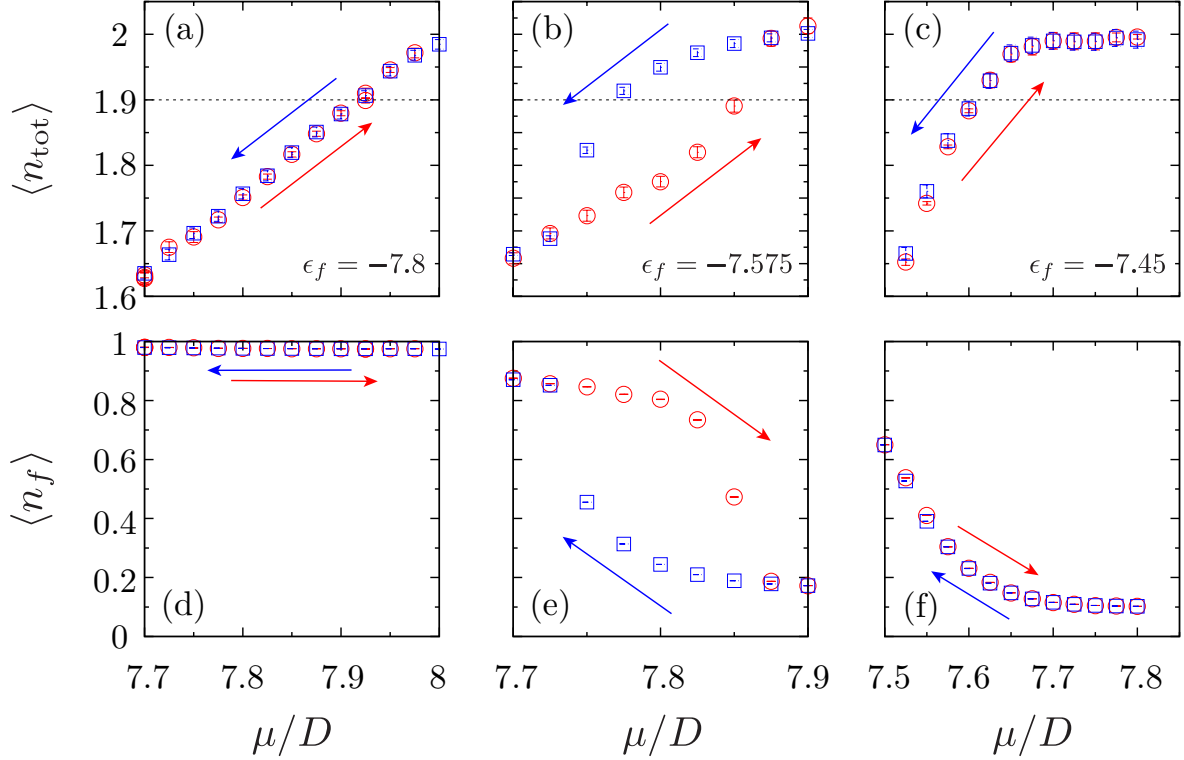


Figure 1. (Color online) The total electron number (upper panels) and f -electron number (lower panels) as functions of the chemical potential in the system with $U_{cf}/D=8$, $V/D=0.13$, and $T/D = 0.04$ when $\epsilon_f/D = -7.8$ (left), -7.575 (middle), and -7.45 (right). The squares (circles) are the data obtained by changing μ from the higher (lower) side.

the mixed-valence state is realized when $7.5 < \mu/D < 7.8$. In the intermediate case with $\epsilon_f = -7.575$, remarkably, the hysteresis appears in the total number of electrons and the f -electron number, as shown in Figs. 1(b) and 1(e). These results indicate the existence of the first-order valence transition in the system with $\epsilon_f/D = -7.575$. In fact, if one considers the system with $\langle n_{\text{tot}} \rangle \sim 1.9$, two solutions are obtained: the Kondo state with $\langle n_f \rangle \sim 1$ and the mixed-valence state with $\langle n_f \rangle \ll 1$.

By performing similar calculations in the system with $\langle n_{\text{tot}} \rangle = 1.9$, we discuss how the f -electron number depends on the energy level of the f -orbital. Figure 2(a) shows the f -electron number at $T/D = 0.04$. When $\epsilon_f/D = -8.0$, the f -electron number is almost one, and the Kondo state with the localized f -electrons is realized. Increasing ϵ_f , $\langle n_f \rangle$ decreases and the first-order valence transition with a jump singularity occurs at $\epsilon_f \simeq -7.575$. Beyond the transition point, the mixed valence state is stabilized with $\langle n_f \rangle \sim 0.2$. As discussed above, we have found two solutions in the case $\epsilon_f/D = -7.575$. Therefore, we can say that the first-order phase transition with the hysteresis indeed occurs between the Kondo and mixed-valence states.

In the vicinity of the valence transition point, the singularity appears in other physical quantities. Fig. 2(b) shows the spin correlation between the conduction and f -electrons $\langle \mathbf{S}_c \cdot \mathbf{S}_f \rangle$. It is found that the $c-f$ spin correlation is enhanced when the system approaches the valence transition point. Then, the jump singularity appears at the first-order transition point. In order to clarify how such singularities in the valence and the spin correlation develop with decrease of temperature, we show in Fig. 3 the temperature dependence of the quantities in the system with $U_{cf}/D = 8.0$ and $V/D = 0.15$. When $T/D = 1.0$, the valence is smoothly varied and

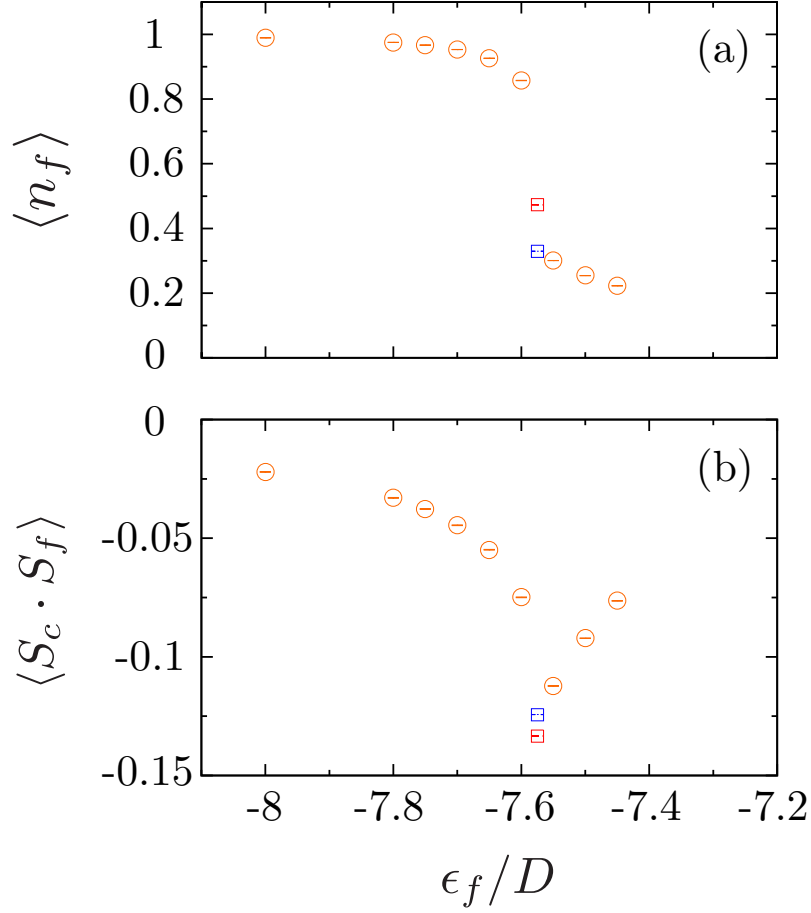


Figure 2. (Color online) f -level dependence of the f -electron number (a) and $c - f$ spin correlation (b) when $T/D=0.04$, $U_{cf}/D = 8$ and $V/D = 0.13$. The squares represent the two solutions at $\epsilon_f/D = -7.575$.

the spin correlation is little changed with increase of the energy of the f -level, as shown in Fig. 3(d). This implies that the high temperature paramagnetic state is realized. The decrease of the temperature leads to the rapid decrease of the valence, as shown in Figs. 3(b) and 3(c). However, we could not find the jump singularity in the valence and thereby a crossover between the Kondo and mixed-valence state occurs. In these cases, interesting behavior appears in the spin correlation, as shown in Figs. 3(d), 3(e), and 3(f). At $T/D = 1.0$, the spin correlation is almost zero and the Kondo singlet state does not appear. Decreasing temperatures, the spin correlation is enhanced around the crossover region at $T/D = 0.33$ and 0.1 , as shown in Figs. 3(e) and 3(f). This indicates that the valence fluctuations enhance the spin correlation between the conduction and the localized f -electrons. Further decrease of temperature induces the valence transition at a certain ϵ_f , where the cusp singularity should appear in the $c - f$ spin correlation. Therefore, it is one of the appropriate quantities to discuss the nature of the valence transitions.

4. Comparison with NCA and OCA results

In this section, we compare the CT-QMC method with the NCA and OCA methods. To this end, we show in the upper panels of Fig. 3 the f -electron number obtained by means of the

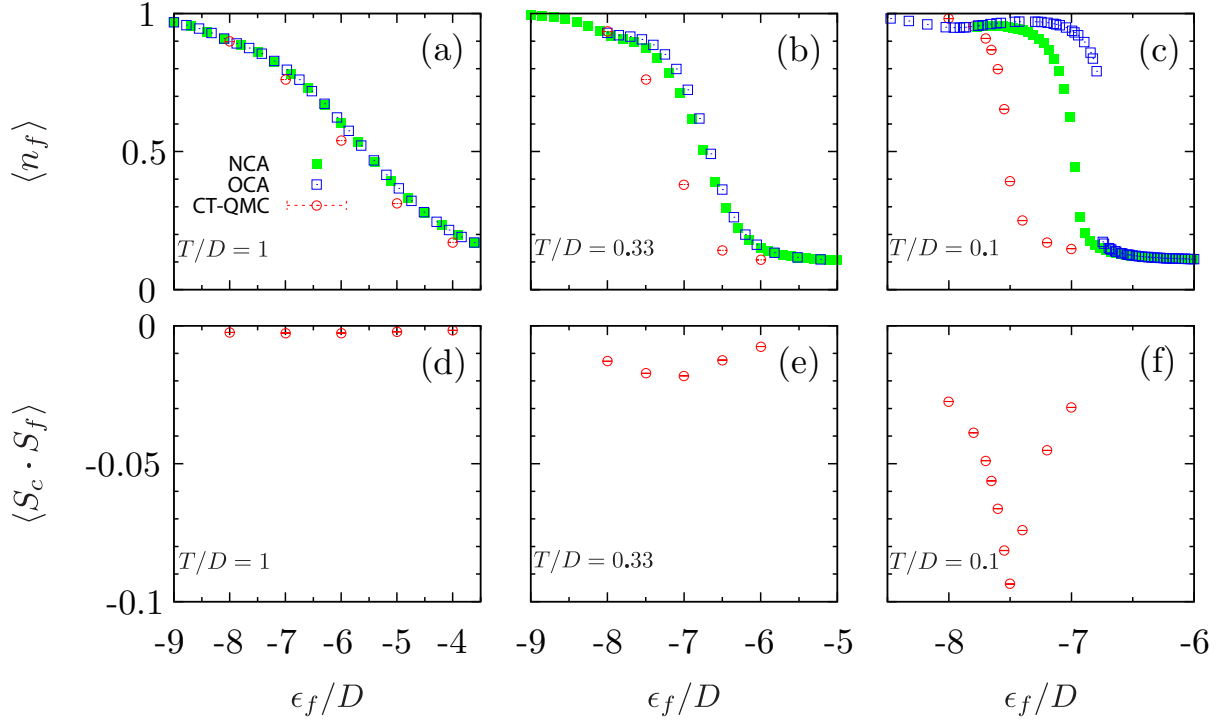


Figure 3. (Color online) The f -electron number (upper panels) and $c-f$ spin correlation (lower panels) in the system with $U_{cf}/D = 8.0$ and $V/D = 0.15$ when $T/D = 1.0$ (left), 0.33 (middle), and 0.1 (right). The open circles, filled squares, and open squares are the results obtained by means of the CT-QMC, NCA, and OCA solvers, respectively.

NCA and OCA solvers. At a higher temperature $T/D = 1.0$, the system is gradually changed from the Kondo like state to the mixed-valence state, as discussed above. In this case, we could not find a big difference in the curves obtained by means of the CT-QMC, NCA, and OCA methods. Therefore, the NCA and OCA methods are appropriate solvers in the case. Decreasing temperatures, slightly different behavior appears, as shown in Figs. 3 (b) and 3(c). We find that the valence crossover points obtained by the NCA and OCA methods are shifted, comparing with that obtained by the CT-QMC method. In addition, when $T/D = 0.1$, a jump singularity in $\langle n_f \rangle$ appears around $\epsilon_f/D \sim 6.75$, which is obtained by means of the OCA method. This valence transition does not appear when the CT-QMC numerical solver is used. Therefore, we can say that the OCA method as well as the NCA method overestimates valence fluctuations at low temperatures.

5. Summary

We have studied the extended periodic Anderson model, combining dynamical mean-field theory with the continuous-time quantum Monte Carlo method. By calculating the f -electron number, we have clarified that at low temperatures, the first-order valence transition occurs between the Kondo and the mixed-valence states together with the hysteresis in the curve of the valence. We have also found that the $c-f$ spin correlation rapidly develops when the system approaches the valence transition point. In addition, The comparison of the impurity solvers such as the CT-QMC, NCA, and OCA has been discussed.

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